ALS SCIENCE HIGHLIGHT

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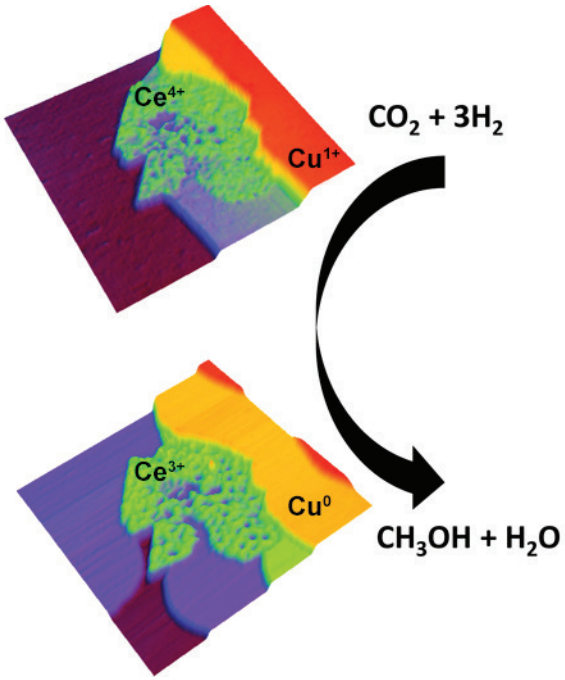
From CO_2 to Methanol via Novel Nanocatalysts

Researchers have found novel nanocatalysts that lower the barrier to converting carbon dioxide (CO_2)—an abundant greenhouse gas—into methanol (CH_3OH)—a key commodity used to produce numerous industrial chemicals and fuels. With the help of ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) at the ALS, researchers have discovered that nanoparticles of cerium oxide (ceria) in contact with copper will form metal–oxide interfaces that allow the adsorption and activation of CO_2, opening a new reaction pathway for the synthesis of methanol. In one case, it worked almost 90 times faster than catalysts commonly used for this reaction today.

Currently, methanol is synthesized industrially from mixtures of H_2 and CO (or sometimes CO_2) at elevated pressures (50 to 100 atm) and temperatures (450 to 600 K) using catalysts containing copper and zinc oxide. The synthesis of methanol from CO_2 is of particular interest as a way to mitigate this abundant greenhouse gas and make use of it as an alternative and economical methanol feedstock. However, because of its chemical inertness, CO_2 interacts only weakly with most catalysts. Previous studies have shown that its reactivity can be enhanced somewhat by "decorating" a Cu surface with Zn or late transition metals. In this work, the researchers took a different approach, coupling Cu to ceria (CeO_x), a reducible oxide. The ceria/Cu system had been studied before as a catalyst for other reactions. The cations of the ceria nanoparticles in contact with Cu can easily alternate between 3+ and 4+ oxidation states. Thus, in ceria/Cu, an active metal–oxide interface can have oxide centers with dynamic chemical properties.

In this study, about 20% of the catalyst's Cu substrate was covered by ceria. The nanostructure was prepared by vapor-depositing Ce onto Cu in an atmosphere of O_2 to form ceria islands on the step edges of a Cu surface. The ceria islands were predominantly



Scanning tunneling microscope image of a cerium oxide (CeO_x) and copper (Cu) catalyst used in the transformation of carbon dioxide (CO_2) and hydrogen (H_2) gases to methanol (CH_3OH) and water (H_2O). In the presence of hydrogen, the Ce^{4+} and Cu^{+1} are reduced to Ce^{3+} and Cu^0 with a change in the structure of the catalyst surface.

Publication about this research: J. Graciani, K. Mudiyanselage, F. Xu, A.E. Baber, J. Evans, S.D. Senanayake, D.J. Stacchiola, P. Liu, J. Hrbek, J. Fernández Sanz, and J.A. Rodriguez, "Highly active copper-ceria and copper-ceria-titania catalysts for methanol synthesis from CO_2," *Science* **345**, 546 (2014).

Research conducted by: J. Graciani and J. Fernández Sanz (Univ. of Seville, Spain); J. Evans (Univ. Central de Venezuela); and K. Mudiyanselage, F. Xu, A.E. Baber, S.D. Senanayake, D.J. Stacchiola, P. Liu, J. Hrbek, and J.A. Rodriguez (Brookhaven National Laboratory).

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U.S. DEPARTMENT OF ENERGY

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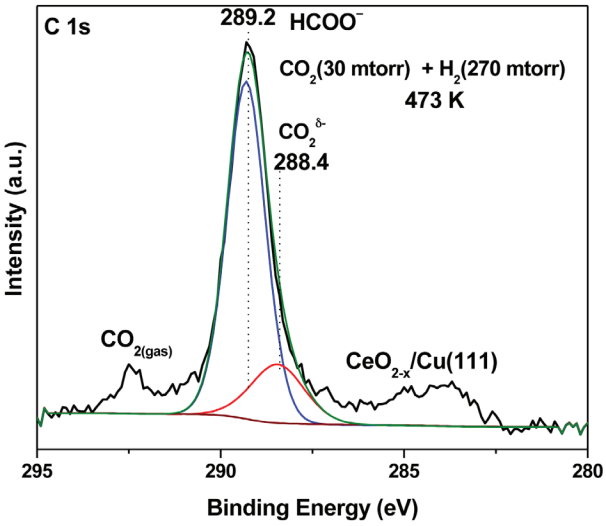
What To Do with CO_2?

Recently, the United States and China announced a joint agreement setting targets for greenhouse gas emissions through the year 2030. It was an acknowledgment, by the world's biggest CO_2 emitters, of the need to address the adverse health and environmental effects of burning fossil fuels. In general, meeting such targets will require multifaceted strategies.

Besides generating *less* CO_2, we can prevent the CO_2 that we *do* generate from lingering in the atmosphere. CO_2 capture and sequestration are familiar examples of this, but there is another facet: CO_2 re-use. Instead of storing CO_2 underground as a waste product, we can "recycle" it into useful products such as chemicals, cements, plastics, or liquid fuels.

For re-use to work, however, the total amount of energy needed to complete a given process must be minimized so that we end up with a net reduction in the CO_2 emitted. Thus, effective catalysts that can lower the energy requirements for CO_2 chemical reactions are an important part of the equation. Here, Graciani et al. report on a new nanocatalyst that can do just that for CO_2 in producing methanol, a key industrial chemical commonly used to make other chemicals and fuels.



C 1s AP-XPS data for a ceria/Cu surface after exposure to CO_2 (30 mTorr) and H_2 (270 mTorr) at 473 K. The weak features at ~284 eV denote the deposition of a very small amount of C on the surface of the catalyst as a consequence of the complete decomposition of CO_2. The main feature can be fitted with two peaks at 289.2 and 288.4 eV, attributed to formates and carboxylates, respectively. The carboxylates were detected in appreciable amounts only when ceria was dispersed on the Cu and were not stable in UHV, making for a better intermediate than the formates.

one layer thick, exhibiting rough surfaces with an occasional CeO_2 termination. Reduction in H_2 increased the surface roughness of the ceria particles, creating an expanded ceria–Cu interface.

Using a combination of AP-XPS at ALS Beamline 9.3.2 and infrared spectroscopy, the researchers investigated the interaction of CO_2 and CO_2/H_2 gas mixtures with Cu, ceria, and ceria/Cu surfaces at temperatures between 300 and 500 K. Pure CO_2 did not adsorb on Cu at these temperatures. On the other hand, the adsorption of CO_2 on a ceria surface produced strongly bound carbonate (CO_3^{2-}) species. A carboxylate ($CO_2^{\delta-}$) species was detected in appreciable amounts only when ceria–copper interfaces were present in the catalyst. The low stability of the carboxylate species makes it an excellent intermediate in the conversion of CO_2 to methanol.

The results of DFT calculations indicated that the thermochemistry of the reaction steps associated with the formation of methanol on a ceria–copper interface is predominantly downhill, with an overall exothermic process.

The researchers also investigated a catalyst generated by co-depositing nanoparticles of Cu and ceria on a substrate of titania (TiO_2). The rate of methanol production for this catalyst was about 87 times faster than for the typical catalyst of copper and zinc oxide in use today, while plain ceria on titania (without Cu) showed no activity for methanol synthesis. The results suggest that the extremely high activity is probably attributable to the type of metal–oxide interface involving Cu and ceria described above.

Dario Stacchiola and Kumudu Mudiyanselage make notes in the data log while Fang Xu (seated) and Jose Rodriguez view microscopic images of the catalyst and Ping Liu and Sanjaya Senanayake adjust the ambient-pressure scanning tunneling microscope. (Photo credit: Brookhaven National Laboratory)

In general, this study illustrates the substantial benefits that can be obtained by properly tuning the properties of a metal–oxide interface in catalysts for methanol synthesis. In a metal–oxide interface, one can have adsorption and reaction sites with complementary chemical properties, truly bifunctional sites that would be very difficult to generate on the surface of pure metal or alloy systems.